EDWIN — A PROGRAM FOR CALCULATING INELASTIC MOLECULAR COLLISION CROSS SECTIONS USING THE EXPONENTIAL DISTORTED WAVE AND RELATED APPROXIMATE METHODS

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PROGRAM SUMMARY

Title of program: EDWIN
Catalogue number: AAJC

Program obtainable from: CPC Program Library, Queens University of Belfast, N. Ireland (see application form in this issue)

Computer: IBM 360/195; Installation: Rutherford Laboratory, Chilton, Didcot, Oxfordshire OX11 0QY, UK
Operating system: IBM system/360 OS
Programming language used: FORTRAN

High speed storage required: 118 K
No. of bits in a word: 8
Overlay structure: none
No. of magnetic tapes required: none
Other peripherals used: disc (optional)

No. of cards in combined program and test deck: 3477
Card punching code: EBCDIC
CPC Library subprograms used: none

References to other published version of this program: none

Key words: inelastic scattering, cross sections, rotationally inelastic scattering, distorted wave, exponential distorted wave, Magnus method, exponential method, Schrödinger equation

Nature of physical problems
EDWIN calculates inelastic molecular cross sections for collisions between an atom and a rigid rotor molecule.

Method of solution
Four approximate methods are available as options, all based upon the distorted wave Born approximation. They are: the distorted wave Born method [1], the centrifugally decoupled distorted wave method [2] and their exponential or unitarised counterparts.
The diagonal channel wavefunctions are propagated from $R$ to $R + kR$ using the Magnus propagation method [3]. At large separations as semiclassical WKBJ form is used.
The contributions to the non-zero distorted wave integrals are accumulated for each propagation interval. By using a phase—amplitude representation of the channel wavefunctions, analytic expressions can be found for these contributions, while each propagation interval may contain many wavelengths without loss of accuracy in the integrals.

Restrictions on the complexity of the problem
The present program treats only atom—linear molecule rotational scattering, but it is reasonably simple to adopt it to other physical problems. There are some limits on the number of channels and the potential which can be easily extended.
The potential should be provided as a Legendre polynomial expansion in the atom—molecule angle. Both the value and first derivative of the $R$-dependent part must be available.

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**Typical running times**
These depend on the various accuracy criteria and the complexity of the problem. Very roughly, the running time goes up with the square of the number of rotational levels. A typical calculation (Ar–N₂, 768 K, 8 rotational levels, 18 total angular momentum values) using the CDEDW method with an accuracy of about 1% requires 3 min on the IBM 360/195.

**Unusual features of the program**
The program is designed around the use of arrays in blank common which are dynamically allocated and whose storage requirements are assigned during execution. In the present version the dynamical storage allocation has been replaced by a single parameter in the main program which the user can set to suit his needs.

**References**

**LONG WRITE-UP**

1. Introduction

Over the past decade sophisticated experimental techniques have been developed to measure inelastic molecular collision cross sections [1]. There has also developed, over this period, a growing interest in vibrational and rotational relaxation rates in gases, which arise from the same cross sections. These relaxation rates are needed in the understanding of relaxation processes in gaseous lasers [2] and of the energy exchange processes occurring in interstellar space [3]. This intense experimental activity has stimulated theoretical efforts to develop viable methods for calculating molecular collision cross sections [4—7]. The exact method of calculating the collision cross sections from an assumed form of the interaction potential is well known [7—10], and is normally referred to as the close-coupling method. This method involves solving sets of coupled differential equations for each total angular momentum quantum number which enters the problem. For typical molecular masses and interaction potentials a very large number of total angular momentum quantum numbers (10²—10³) must be considered and for each value of the total angular momentum quantum number a set of coupled differential equations of very large dimensionality (10²—10³) must be solved. The computational intractability of the close coupling method for typical molecular systems at all but the lowest energies has led to the development of many approximate computational schemes [4,5,7,11—16]. The principle aim of all these schemes is, in some way or other, to decouple the large set of coupled differential equations.

One of the oldest approximate methods of scattering theory is the distorted wave Born approximation [7,9,17]. In this method the terms which couple the differential equations are at first ignored. The uncoupled differential equations are solved to yield “distorted waves”, and the integrals of the coupling terms between the distorted waves (the distorted wave integrals) are then evaluated and used to provide a perturbation theory estimate of the cross sections. The distorted wave integrals are often difficult to evaluate because of the highly oscillatory behaviour of their integrands. In the present program we overcome this difficulty by using a phase—amplitude representation of the distorted waves or channel wavefunctions. This representation of the channel wavefunctions enables us to formulate valid analytic expressions for the contributions to the distorted wave integrals from each increment in the variable of integration (R). The increments in R often extend over many wavelengths of the channel wavefunctions. The channel wavefunctions themselves are evaluated by solving the uncoupled Schrödinger equations for each channel using the exponential or Magnus propagation procedure [18]. At large R, where the potential is weak, a semiclassical JWKB form of the method is used which permits very large steps to be taken in the propagation of the wavefunction.

The program is constructed to calculate cross sections for the rotationally inelastic scattering of an atom and a rigid-rotor diatomic molecule, with neither of the collision partners possessing any additional degrees of freedom. It can easily be modified to handle more general situations such as diatom—diatom scattering or vibrationally
in elastic processes. The program has options within it to perform several kinds of calculation based on the use of the distorted wave integrals. Firstly there is the standard distorted wave Born (DW) approximation. This approximation suffers from the fact that it does not yield a unitary $S$ matrix and therefore fails to conserve particle flux. A useful method of increasing the validity of the distorted wave Born approximation has been shown to be the exponential distorted wave (EDW) approximation $[7,19,20]$ in which the distorted wave integrals are exponentiated to yield an intrinsically unitary form of the $S$ matrix. The EDW approximation is the second optional method used within the program for the calculation of inelastic cross sections. Both the DW and EDW approximations are based on the use of a space-fixed coordinate system. The basic coupled differential equations of scattering theory may also be formulated within a body-fixed axis system $[21]$. Starting from this formulation of the problem it is possible to realise great simplifications by neglecting the coupling terms arising from the orbital angular momentum operator $[11,12]$. We refer to the neglect of these terms as centrifugal decoupling. Recently, further simplifications to this widely used approximation have been suggested $[16]$. These new approximate schemes treat the residual coupling within the body-fixed differential equations using either straightforward perturbation theory CDDW or a unitarised (exponential) perturbation theory CDEDW. Both of these methods are also available as options within the program.

2. Theory

2.1. Space-fixed coordinates – the Distorted Wave (DW) and Exponential Distorted Wave (EDW) approximations

By expanding the wavefunction in eigenfunctions of the total angular momentum ($J$) we obtain $[7,9]$ from the time independent Schrödinger equation for atom–rigid rotor diatom scattering, the following set of coupled differential equations for each value of the total angular momentum:

$$\left[ \frac{d^2}{dR^2} + \kappa_J^2 \right. - \left. \frac{l(l+1)}{R^2} - U_{J,J',J''}^{J',J'',J}(R) \right] \psi_{J,J',J''}^{J',J'',J}(R) = \sum_{J'''' J'''} U_{J,J'',J'''}^{J',J'',J}(R) \psi_{J,J'',J'''}^{J',J'',J}(R),$$

where:

$$\kappa_J^2 = \frac{(2\mu \hbar^2)}{2I} \left[ E - J(J+1) \hbar^2 / 2I \right],$$

$U_{J,J',J''}^{J',J'',J}(R)$ are the matrix elements of the potential between eigenfunctions of the total angular momentum $[7,9,10]$, $E$ is the scattering energy measured relative to the $j=0$ rotational state and $I$ is the moment of inertia of the diatomic molecule. The principle of conservation of parity results in the uncoupling of the differential equations into two sets, one with $(J'+J'')$ even and the other with $(J'+J'')$ odd $[22]$.

In the distorted wave (DW) approximation the inhomogeneous part on the right hand side of eq. (1) is treated as a perturbation. We therefore first solve the uncoupled homogeneous equations to find the distorted waves $\phi_{J,J}(R)$:

$$\left[ \frac{d^2}{dR^2} + \kappa_J^2 - \frac{l(l+1)}{R^2} - U_{J,J,J}^{J,J,J}(R) \right] \phi_{J,J}(R) = 0$$

with boundary conditions:

$$R \phi_{J,J}(R) \sim 0, \quad R \rightarrow 0,$$

$$\phi_{J,J}(R) \sim \sin(k_J R - ln/2 + \eta_J), \quad R \rightarrow \infty,$$
where \( \gamma \) are the phase shifts. Having found the distorted waves we must then evaluate the distorted wave integrals and the so-called \( A \) matrix.

\[
A_{f',f;ij} = 0,
\]

\[
A_{f',f;ij} = \frac{-2}{(2f+1)!} \int_{0}^{\infty} \phi_{f'}(R) U_{f',f;ij}(R) \phi_{ij}(R) \, dR \quad \text{if} \neq \text{f'}.
\]  

(5)

The \( S \) matrix in the distorted wave approximation is then given by:

\[
\text{DW approximation } \quad S_{f'f;ij} = e^{i\eta_{f'}\phi'} \left[ \delta_{f',f;ij} + iA_{f',f;ij} \right] e^{i\eta_{ij}}.
\]  

(6)

In the unitarised exponential distorted wave approximation it is given by:

\[
\text{EDW approximation } \quad S_{f'f;ij} = e^{i\eta_{f'}\phi'} \left[ e^{iA} \right]_{f'f;ij} e^{i\eta_{ij}}.
\]  

(7)

Once the \( S \) matrices have been evaluated the required cross sections are calculated using standard formulae:

\[
\sigma_{f'f} = \frac{\pi}{k_{f}^{2}(2f+1)} \sum_{f'} (2f+1) \sum_{ij} |\delta_{f',f;ij} - S_{f'f;ij}|^{2}.
\]  

(8)

The program also evaluates (if requested) the dimensionless partial cross sections defined by the formula:

\[
P_{f'f} = \frac{(2f+1)}{(2f'+1)} \sum_{ij} |\delta_{f',f;ij} - S_{f'f;ij}|^{2}.
\]  

(9)

2.2. Body-fixed coordinates — the Centrifugally Decoupled Distorted Wave (CDDW) and the Centrifugally Decoupled Exponential Distorted Wave (CDEDW) approximations

In the body-fixed coordinate system the basic set of coupled differential equations take the form [12,23]:

\[
\left[ \frac{d^{2}}{dR^{2}} + k_{f}^{2} - \frac{C_{\Omega f',\Omega}^{\Omega'} R^{2}}{2} U_{f',f;ij}(R) \right] \psi_{f'}^{\Omega'}(R) = \frac{C_{\Omega f',\Omega'}^{\Omega'} R^{2}}{2} \psi_{f'}^{\Omega'}(R)
\]

\[
+ \frac{C_{\Omega f',\Omega+1}^{\Omega+1} R^{2}}{2} \psi_{f'}^{\Omega+1}(R) + \sum_{f' \neq f'} U_{f',f;ij}(R) \psi_{f'}^{\Omega'}(R) \psi_{f'}^{\Omega'}(R),
\]  

(10)

where the helicity quantum numbers \( \Omega \) correspond to the projection of the total angular momentum onto the body-fixed z axis. The centrifugal decoupling approximation involves neglecting the off-diagonal matrix elements of the orbital angular momentum operator — i.e. the coupling terms involving \( C_{\Omega f',\Omega-1}^{\Omega'} \) and \( C_{\Omega f',\Omega+1}^{\Omega'} \) on the right hand side of eq. (10). This approximation is also used in the popular coupled states (CS) [11] and p-helicity decoupling [12] methods. After neglecting these coupling terms there still remain the coupling terms arising from the interaction potential (i.e. the \( U_{f',f;ij}(R) \) terms). This residual coupling is treated using the distorted wave or exponential distorted wave approximations.

Thus to determine the distorted waves we solve the uncoupled differential equations:

\[
\left[ \frac{d^{2}}{dR^{2}} + k_{f}^{2} - \frac{C_{\Omega f'}^{\Omega} R^{2}}{2} U_{f;ij}(R) \right] \phi_{ij}(R) = 0
\]  

(11)
with boundary conditions:

\[ R \phi_{j\Omega}(R) \sim 0, \quad R \to 0 \]
\[ \phi_{j\Omega}(R) \sim \sin(k_j R - \ln 2 + \eta_{j\Omega}), \quad R \to \infty \]

where the number \( l \) is determined in such a way that:

\[ l(l + 1) = C_{j\Omega}^2 = J(J + 1) + j(j + 1) - 2\Omega^2. \]

Using the distorted waves we then calculate the \( A \) matrix:

\[ A_{j'}^{j} = \frac{-2}{(k_j k_{j'})^{1/2}} \int_0^\infty \phi_{j\Omega}(R) U_{j'}^{j}(R) \phi_{j\Omega}(R) \, dR, \quad j' \neq j. \]

The \( S \) matrix may then be evaluated using either a distorted wave or exponential distorted wave approximation.

**CDDW approximation**

\[ S_{j',j}^{j\Omega} = e^{i\eta_j \Omega} \delta_{j'}^{j} + i A_{j'}^{j\Omega} \ e^{i\eta_j \Omega}, \]

**or**

**CDEDW approximation**

\[ S_{j',j}^{j\Omega} = e^{i\eta_j \Omega} \ e^{iA_{j'}^{j\Omega}}. \]

The equations and \( S \) matrices for positive and negative \( \Omega \) are equal within the centrifugally decoupled approximation and need therefore only be calculated for \( \Omega \geq 0 \). The cross section is then given within this centrifugally decoupled formalism by the formula [12]:

\[ \sigma_{j'-j} = \frac{k_j}{\pi} \sum_{\Omega} (2J + 1) \sum_{\Omega'} |S_{j',j}^{j\Omega}|^2 \]

and the dimensionless partial cross section is given by:

\[ P_{j'-j} = \frac{(2J + 1)}{(2j + 1)} \sum_{\Omega} |\delta_{j,j} - S_{j,j}^{j\Omega}|^2. \]

The program will also print out, if requested, the partial partial cross sections (i.e. the contributions to the partial cross section from each helicity (\( \Omega \)) quantum number).

As stated above the helicity quantum number \( \Omega \) corresponds to the projection of the total angular momentum onto the body fixed \( z \) axis. As the \( z \) component of the orbital angular momentum is zero in the body fixed axis system, \( \Omega \) also corresponds to the projection of the rotational angular momentum onto the body fixed \( z \) axis. Thus for a particular \( j \to j' \) rotational transition only \( \Omega \) values less than or equal to the smaller of \( j \) and \( j' \) contribute. Thus in the summation over \( \Omega \) in eq. (17) we need not include values of \( \Omega \) greater than the \( j_{\text{fin}} \), where \( j_{\text{fin}} \) is the maximum value of the smaller of \( j \) and \( j' \) for all transitions of interest.

### 2.3. The potential and its matrix elements

The potential must be given in the traditional manner [7,8,10,23] as an expansion in Legendre polynomials of cosine of the atom–diatom angle

\[ V(R, \theta) = \sum_{\lambda} V_\lambda(R) P_\lambda(\cos \theta). \]
The program evaluates the matrix elements of such a potential in a basis set corresponding either to the space-
fixed or the body-fixed coordinate system as required. The relevant formulae for the matrix elements are:

**Space-fixed coordinate system**

\[ U_{J_1 J'1'}(R) = \sum_\lambda V_\lambda(R) f_\lambda(J_1, J' 1'; J) \frac{2\mu}{\hbar^2}, \tag{20} \]

where the Percival—Seaton coefficients \( f_\lambda \) have been extensively discussed in the literature \([7,8,10]\).

**Body-fixed coordinate system**

\[ U_{J_2 J'2}^P(R) = \sum_\lambda V_\lambda(R) \left( \frac{2J_1 + 1}{2J' + 1} \right)^{1/2} C(J_2 J_1' | 000) C(J' J_2' | 000) \frac{2\mu}{\hbar^2}, \tag{21} \]

where the \( C \)'s are Clebsch–Gordan coefficients \([12,23]\).

### 3. Program

#### 3.1. Introduction

The program is written in Fortran IV and has been running on the IBM 360/195 computer at the Rutherford
Laboratory. All floating point operations are performed in double precision. When run on the Rutherford
Laboratory computer, the program uses a facility to allocate array dimensions dynamically. As this facility is
not generally available on other computers, we have replaced it with a single “size” parameter in the main pro-
gram, which can be set by the user to his own requirements. The program contains many comment cards and the
purpose of each subroutine is described in its first comment statements. The meaning of the common variables is
described in comment cards in the Block Data subprogram.

#### 3.2. Solution of the uncoupled channel differential equations

Each of the diagonal channel wavefunctions, see eqs. (3) and (11), is propagated over incremental intervals in
the scattering coordinate \( R \). After each propagation step contributions to all the non-zero distorted wave integrals
are accumulated. The propagation of the wavefunctions over each interval is carried out using the exponential
method of Magnus as described by Chang and Light \([18]\). The starting point \( (R_0) \) for the integration of each
channel is determined by the requirement, see eq. (IV.8) of ref. \([18]\):

\[ \int_{R_0}^{R_{TP}} |p| \, dR \approx |p(R_0)|^2 (R_{TP} - R_0)^2/4 = 2.3\delta, \tag{22} \]

where \( \delta \) is input as data to the program, \( R_{TP} \) is the classical turning point distance and \( p(R) \) is the local wavevec-
tor, see ref. \([18]\) eq. (II.1). Increasing the value of \( \delta \) makes \( R_0 \) decrease. At \( R_0 \) the amplitude of the wavefunction
is set to the initial value of \( 10^{-20} \), in order to allow it to grow considerably without causing overflow problems.
If the amplitude nevertheless exceeds \( 10^{+20} \) in the propagation process, the wavefunctions are renormalised
and a warning is printed. However, our experience has shown that using the default value for \( \delta (30.0) \) the amplitudes
reach a value of only \( 10^{-13} \). The phase of the wavefunction (see section 3.3 below) at the starting point is deter-
mained using a somewhat more accurate formula than that of Chang and Light, i.e.

\[ \theta(R_0) = \tan^{-1}\left[ k/|p(R_0)| - \frac{1}{2|p(R_0)|} \frac{d|p|}{dR} \right]. \tag{23} \]
The propagation of the wavefunction is done using the second Magnus approximation, ref. [18] eq. (II.14). The integrals needed to evaluate the "translation matrix" or "propagator" are evaluated using a piecewise cubic Hermite approximation [24]. This involves the evaluation of the channel potential and its derivative at both ends of the interval over which the wavefunction is being propagated.

The accuracy of the propagation is determined by a variable "EPS" which is input as data. The precision of the propagation is continuously monitored by first propagating each channel wavefunction over the current step-length "h" and then propagating the wavefunction over the same interval in two steps of length h/2. The maximum error in the phase of the wavefunction is then used to set a new step-length using the recipe:

$$h_{\text{new}} = h_{\text{old}}(\text{EPS} \times 10^{-4}/\text{ERROR})^{1/4}.$$  

Although "EPS" is the major parameter in determining the accuracy of the cross sections, other factors (δ, the integration range, use of the WKBJ approximation etc.) also have a considerable influence. With the defaults set in the program (EPS = 0.002) a relative accuracy in the partial cross-sections of better than 1% may be expected if no WKBJ approximation (see below) is used.

It should be noted that the program permits the step-length of a single propagator step to be larger than the wavelength of the wavefunction. Indeed, if this were not possible the whole procedure would become very inefficient especially at high collision energies.

If requested by the relevant input data the program uses a WKBJ propagator at large distances, see ref. [18] eq. (11.11). The criterion for switching from the exact to the WKBJ propagator is

$$|\frac{dp}{dR}/2p^2| \leq \text{CWKBJ},$$  

where p(R) is the local wavevector, see ref. [18] eq. (II.1), and CWKBJ is provided as data to the program. Using the WKBJ propagator this way, with CWKBJ set to its default value of 0.01, the partial cross sections are obtained with a numerical accuracy of better than 2%.

### 3.3. The phase-amplitude representation of the channel wavefunction and the evaluation of the distorted wave integrals

With a view to simplifying the evaluation of the distorted wave integrals, the channel wavefunctions are re-expressed in a phase–amplitude representation. That is, we write the wavefunction in the form:

$$\phi(R) = A(R) \sin(\theta(R))$$  

its derivative can be written as [25]

$$\frac{d\phi(R)}{dR} = kA(R) \cos(\theta(R)),$$  

where k is the wavevector, see eq. (3) and (11). Therefore the amplitude is obtained using:

$$A(R) = \left[ (\phi(R))^2 + \left( \frac{1}{k} \frac{d\phi(R)}{dR} \right)^2 \right]^{1/2}$$  

and the phase is given by:

$$\theta(R) = \tan^{-1}[k\phi(R)/d\phi/dR].$$  

Thus, the amplitude and the phase of the wavefunction may readily be evaluated from the wavefunction and its derivative. Some problems arise because eq. (29) only determines the phase modulo-pi and we require to know its absolute value. This problem is resolved by using a semiclassical estimate of the change in the phase of the wavefunction over a single propagation step, to add on the correct multiple of pi where necessary.

In the evaluation of the distorted wave integrals we also require the first derivative of the amplitude. Using
eqs. (26) and (29) and the Schrödinger equation for the channel wavefunction one can show that:

\[ \frac{dA}{dR} = \left[ U(R)/2k \right] A(R) \sin(2\theta(R)), \]

where \( U(R) \) is the effective channel potential [i.e. \( U(R) = l(l+1)/R^2 + U_{l,n}(R) \) in the space-fixed coordinate system, see eq. (3)].

The contributions to the distorted wave integrals, which we wish to evaluate are of the form:

\[ D_{12} = \int_a^b \phi_1(R) U_{12}(R) \phi_2(R) dR. \]

Using the phase-amplitude representation of the wavefunctions, eq. (31) can be rewritten in the form:

\[ D_{12} = \int_a^b g(R)[\cos(\theta_1(R) - \theta_2(R)) - \cos(\theta_1(R) + \theta_2(R))] dR. \]

where \[ g(R) = \frac{1}{2} A_1(R) U_{12}(R) A_2(R). \]

The function \( g(R) \) is approximated analytically by using the piecewise cubic Hermite interpolation procedure [24]. The value and derivative of \( g(R) \) at both ends of the integration interval, which are needed for this, are obtained using the formulae quoted above and the equation:

\[ \frac{dg}{dR} = \frac{1}{A_1} \frac{dA_1}{dR} + \frac{1}{U_{12}} \frac{dU_{12}}{dR} + \frac{1}{A_2} \frac{dA_2}{dR}. \]

The phases \( \theta_1(R) \) and \( \theta_2(R) \) are approximated as linear functions over the integration interval. With these approximations the contributions to the distorted wave integrals from a given interval may be evaluated analytically.

### 3.4. The exponentiation of the \( A \) matrix

In order to obtain a unitarity \( S \) matrix in the exponential distorted wave methods we have to compute the matrix \( e^{iA} \), see eqs. (7) and (16), where \( A \) is the matrix of distorted wave integrals, eqs. (5) and (14). For this purpose we use the following relation:

\[ e^{iA} = a e^{i\lambda} a^+, \]

where \( a \) is the eigenvector matrix of \( A \) and \( e^{i\lambda} \) is a (complex) diagonal matrix with diagonal elements \( e^{i\lambda_j} \), while \( \lambda_j \) is the eigenvalue corresponding to the \( j \)th eigenvector of \( A \). Since \( A \) is a symmetric real matrix, its diagonalisation may be performed by any of the generally available standard routines.

### 3.5. Summation over the total angular momenta

The calculation of the integral cross sections, eqs. (8) and (17), involves the summation over partial cross sections corresponding to a wide range of total angular momentum values. Usually the partial cross sections are a reasonably smooth function of \( J \). This permits us to treat this summation as an integral, requiring much fewer total angular momenta to be considered. Since the abscissae (the total \( J \) values) are restricted to integer values, the Newton–Cotes quadrature schemes [26] are particularly suited for the integration. The standard scheme used is the Simpson rule, which is applied repeatedly if necessary. In special cases the trapezium or the 3/8 rules are employed, i.e. the trapezium rule is used if only two total \( J \) values are involved, while the 3/8 rule applies to the last four abscissae if an even number of points is specified.
Using these quadrature schemes a 20–40 total angular momenta are usually enough to yield integral cross sections which are converged to within 1%. Note that the replacement of the summation by an integral is only valid when a reasonably large number of total angular momentum quantum numbers are involved. If one wishes to consider all the total angular momentum values (i.e. JTSTEP = 1 in the input data) the program naturally performs the simple summation from eqs. (8) and (17).

### 3.6. The size parameter

In the main program the statements COMMON CR(3000) (card 21) and NCORE = 3000 (card 34) appear. The number “3000” appearing in these two cards can be changed to suit the requirements of the problem being investigated. Table 1 indicates the value of the parameter “NCORE” needed for some typical problems and also the (estimated) core size needed by the program.

The program tests the value of NCORE and prints a message concerning the actual number of words used. If NCORE is not large enough the calculation is aborted (stop 2). The user who wants to use his own locally supplied routines for dynamical core storage finds all information he needs in subroutines MAINCS and FRMAIN.

### 3.7. Structure of the program

A diagram of the subprograms is given in fig. 1 where the manner in which they are called is also indicated. The purpose of most routines should be clear from their first few comment cards. Still the following should be noted:

**FGO1BD** This function is copied with permission from the Harwell Subroutine Library. It evaluates the Clebsch–Gordon coefficients \( C(\lambda,|\Omega|\Omega 0 \Omega 2) \) needed in the matrix-elements over the potential in the body-fixed coordinate system, see eq. (21). In the present version the sum of the three angular momenta appearing in any “triangular condition” may not exceed 100.0. This limit can be raised by using larger dimensions for the assays H and J (card 919) and a correspondingly larger limit on the index of the do-loop (card 989).

**FRACAH** This subroutine also includes the functions AF and DELTA and was originally written by: B.R. Johnson, Ohio State University. It evaluates the Percival–Seaton coefficients needed in the matrix-

### Table 1

Number of words of blank common and core usage needed for some typical CDEDW calculations (with the EDW numbers in parentheses)

<table>
<thead>
<tr>
<th>( f_{rot} )</th>
<th>NCORE</th>
<th>estimated core usage in bytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>202 (388)</td>
<td>98 K (100 K)</td>
</tr>
<tr>
<td>10</td>
<td>289 (3319)</td>
<td>100 K (122 K)</td>
</tr>
<tr>
<td>20</td>
<td>654 (31564)</td>
<td>102 K (340 K)</td>
</tr>
<tr>
<td>30</td>
<td>1169 (135809)</td>
<td>106 K (1160 K)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( f_{rot} )</th>
<th>NCORE</th>
<th>estimated core usage in bytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>380 (1375)</td>
<td>102 K (110 K)</td>
</tr>
<tr>
<td>10</td>
<td>929 (17068)</td>
<td>106 K (230 K)</td>
</tr>
<tr>
<td>20</td>
<td>2084 (160193)</td>
<td>116 K (1350 K)</td>
</tr>
<tr>
<td>30</td>
<td>3649 (604193)</td>
<td>128 K (4820 K)</td>
</tr>
</tbody>
</table>
elements over the potential in the space-fixed coordinate system, eq. (20). It has the same kind of limitations as FG01BD but unlike that routine it aborts (stop 999) and prints an informative message if the limit is exceeded. Change cards 1682 and 1683 in that case.

**GIVENS** This routine for the diagonalisation of a matrix is a slightly adapted version of program 62.3 distributed by QCPE [27].

**TIMING** Since this routine has many calls to system dependent features it is completely transformed into a comment.
MAINCS This function mimics the dynamical core storage. It includes routine FRMAIN.
MAIN The first executable statement (card 28) is a call to ERRSET in order to suppress underflow messages on the IBM 360/195.

A normal calculation proceeds as follows. Firstly, the input is read and processed by DWIN which also determines the partitioning of blank common. Then CDEDW is called to compute the cross sections. For each energy ELEVEL computes the channel energies and the total cross sections are calculated in a loop over all selected total angular momentum values, using the quadrature weights selected by QUAD. Each partial cross section is a sum of partial—partial cross section corresponding to odd or even parity ((E)DW methods) or a helicity quantum number (CD(E)DW methods). To compute these partial—partial cross sections firstly CBASIS is called to select BASIS (body fixed) or BASISS (space fixed), and to determine which quantum numbers, centrifugal barriers and potential coupling coefficients are to be used. Then TMAT computes the T matrix (i.e. S—I) using ACTION to compute the A matrix and phase shifts following the methods described in sections 3.2 and 3.3. ATOS or EXPA is called to obtain the S matrix from the A matrix. The S matrix is printed by WRITER if requested in the input data. Finally the T matrix elements are quadratically summed (CROSS) to yield the cross sections. These may then be printed using WRITEC.

4. Use of the program

Two kinds of input need to be specified, i.e. the potential via the subroutine VMAT and the other input using normal card input.

4.1. The potential

The potential must be specified as an expansion in Legendre polynomials (see section 2.3):

\[ V(R, \theta) = \sum_{\lambda} V_{\lambda}(R) P_{\lambda}(\cos \theta) \]  

(19)

It should be provided for each system to be studied as:

SUBROUTINE VMAT (R, V, DV)

(see card 518 and following), yielding for each distance R the value (V) and first derivative (DV) of the radial component \( V_{\lambda}(R) \).

Not all values of \( \lambda \) need to be present, e.g. for Ar—N\(_2\) only even \( \lambda \)'s were used, but this must be indicated in the card-input (LAMIN, LAMAX, LASTEP). However, the first term (V(1), DV(1)) should always give the isotropic part of the potential.

Note that the potential can be manipulated somewhat using the card input (NANIS, ANIS; RSCALE, VSCALE).

** If the potential expansion contains more than 99 terms the number 100 on card 296 should be changed to at least 1 more than the number of terms.

4.2. Card input

Data card 1

Title,
this card is completely reproduced in the output.

Data card 2

Namelist CDEDW,
defaults have been assigned to most variables. Only RMASS, EROT and ETOTAL must be specified. The defaults are shown in square brackets.
LCD[1]  Determines which approximation is used according to:
1  CDEDW  −1  EDW
2  CDDW  −2  DW

EPS[0.002]  Accuracy (see section 3.2), the percentage error is \( \approx \text{EPS} \) for \( 0.1 < \text{EPS} < 0.001 \).

KOPT[1]  Controls the amount of print output:
\( \leq 0 \)  control and input data, energy levels and rotational quantum numbers
1  partial cross sections
2  core partitioning,
   details concerning rotational basis,
   \( A \) matrices, phase shifts, \( S \) matrices,
   partial—partial cross sections.
3  potential coupling coefficients,
   Information about propagation,
   Renormalised \( A \) matrix and channel-amplitude (if necessary).
4  results for each step in search for classical turning point,
   results for each propagation step.
8  details from distorted wave integral computation per propagation step.

RMASS  Reduced mass in chosen units = \((1/\text{atom mass} + 1/\text{molecule mass})^{-1}\).

EROT  Rotational B constant for molecule,
\( \text{EROT} = \hbar^2/2\mu \gamma_0^2 \) where \( \mu \) and \( \gamma_0 \) are the reduced mass and the equilibrium distance for the diatom.

HBAR[1.0]  \( \hbar \) in chosen units.

ETOTAL  Total energy (with respect to \( j_{\text{rot}} = 0 \))

EMIN[ETOTAL]  Minimum total energy used.

NESTEP[0]  Number of steps taken between EMIN and ETOTAL.

JTMIN[JTMAX]  Minimum, maximum and stepsize for the total angular momentum value.

JTMAX[50]  \( J_{\text{rot}} \) cutoff for each step in search for classical turning point.

JSTEP[1]  \( J_{\text{rot}} \) step size for each propagation step.

JROMIN[0]  Minimum, maximum and stepsize for rotational quantum number
(\( \text{JSTEP} \) should be 1 for a heteronuclear diatom and may be 2 for a homonuclear one).

JROMAX[0]  \( J_{\text{rot}} \) cutoff for each propagation step.

JRSTEP[MAXO(LASTEP, 1)]  ** only applicable to the CD(E)DW approximations ** Maximum
value of \( \Omega \) used in summation over partial—partial cross sections, only
cross section for excitations to or from maximal \( \text{JRFIN} \) are valid, this
option might save a considerable amount of computer time.

JRFIN[JROMAX]  Minimum (excluding 0), maximum and stepsize for the value of \( \lambda \) in
the Legendre expansion for the potential (see section 4.1),
\( \text{NP} \) is the number of terms in the potential, which is determined by
function \( \text{NPOT} \) (card 491 etc.);
note: \( \text{LAMAX} \) may be specified as less than \( \text{NP} \) in which case not all
the terms in the potential will be used.
LWKBJ[1] 1  WKBJ approximation is used where appropriate, 0  no WKBJ used.
CWKB[0.01] Criterion for start of WKBJ propagation, eq. (25).
RScale[1.0] Distance scaling factor.
VScale[1.0] Energy scaling factor.
  i.e. These scaling factors correspond to the units used in VMAT expressed in terms of the units used in the input. The numbers input to the program as data are divided by these scale factors before use thus converting them to reduced units (see CONV and CONVP).
CONV[RScale**2] Factors to multiply the integral and partial corrections.
CONVP(CONV) (The default yields the cross sections in the units used in the namelist input). The value 0.0 yields the dimensionless cross section, eqs. (9) and (18).
RBEG[2.0] Starting point for search for innermost turning point. A warning is printed if the propagation starts at a distance smaller than RBEG.
REND[45.0] End of propagation range.
DFACT[30.0] $\delta$ used in determining start for propagation, see eq. (22).
JMAX[250] Maximum number of steps in search for innermost turning point.
LOPT[1] $\leq$0 Only propagation of channel wavefunctions. $>$0 Distorted wave integrals are computed.
IDISC[0] if IDISC $\neq$ 0 all $S$ matrices are written into unit IDISC.
NANIS[0] Number of anisotropy parameters which must be changed from their default value of 1.0 (see ANIS; card 3).
  Data Card 3 (Only if NANIS > 0). ANIS(I), I = 1, NANIS[8D10.3] The (I + 1)th potential term is multiplied by ANIS(I).

When the calculation is completed the program tries to read data for the next one. If no data cards are found the program exits.

4.3. Output

A few pages are shown from a test run for the Ar—N$_2$ system where the print flag KOPT is rather high. Most output is self-explanatory. The big letters on top of the first page indicate the approximation used. The interaction potential used was taken from M.D. Pattengill, R.A. LaBudde, R.B. Bernstein and C.F. Curtiss, J. Chem. Phys. 55 (1971) 5517.

Acknowledgements

We thank Mr. C. Bocchetta for assisting with some of the programming. We thank the S.R.C. for financial assistance and for the provision of computer time on the Rutherford Laboratory computer. J.H. van Lenthe
thanks the Ramsay Memorial Trust for the provision of a Fellowship. We thank Harwell computing division for permission to include the source of the subroutine FG01BD in the present program.

References

[27] H. Michels and F. Prosser, QCPE 11 (1965) 62; Givens subroutine available from Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, IN 47401, USA.
TEST RUN OUTPUT

Several pages have been omitted between pages 1 and 2

---

** LIMITS ON FRATIONAL ODD E's: JMIN = 0 JMAX = 10 JSTEP = 2 **

** CROSS SECTIONS ONLY VALID FOR INITIAL OP J-FINAL LESS OR EQUAL 16 JFIN = 0 **

** TOTAL ENERGY = 1.2585000000+01 (= 0.2500000000+01 REDUCED) **

** TOTAL ANGULAR M.R. LIMITS, JMIN = 00 JMAX = 100 JSTEP = 20 **

** // POTENTIAL // : ELASTIC PART (U0) + LAMAX = 2 LAMAX = 2 IN STEPS OF 2 **

** (TOTAL NUMBER OF TIPS: 1000) **

** ENERGY/DISTANCE SCALING: }MM = 0.64855230F+01 RSCALE = 0.0500000000E+01 VSCALE = 0.1250000000E+01 **

** SCALE-FACTORS FOR TOTAL AND PARTIAL CROSSECCTIONS RESPECTIVELY: } 0.1250000000E+00 / 0.0 **

** (A .001 VIDE THE DIMENSIONLESS CROSSSECTION) **

** REDUCED TASKS : 0.19479533D+02 (= 8890 = 1.744235230D+23) **

** ROTATIONAL L-CONSTANT : E00 = 0.1400000000E+03 (IS 0.267477571-C1 REDUCED) **

** INTEGRATION RANGES : RMIN = 0.2500000000E+01 (0.71429478E+00 REDUCED) RMAX = 0.71429478D+02 (0.1257415002 REDUCED) **

** SPACE = 0.125000 **

** // OPTIONS KEPT : 1 LEFT : 1 INDISC : 0 ICD : 1 **

** // A WKB-PROPAGATOR IS USED AS SOON AS P**2/4**2 < 0.16000000-C1 **

** // **

** *** THE PRECISION (EPS) IS 0.02-C02 ***

** KASS : 0 KTOTAL : 3 K' : 59 KDV : 65 KSCR : 65 **

** KS0 : 176 KS1 : 204 KSA : 71 KPS : 78 **

** KCPJ : 65 KCJUL : 176 KETA : 212 **

** NUM : 7 NCR : 1 NCR : 1 NNC : 1 NNC : 2 **

** MLCPJ : 13 MLSCR : 99 **

---

** THIS RUN REQUIRES 289 WORDS OF ELANK COMMON (8 BYTES / BK) **

---

G.G. Balint-Kurti et al. / EDW\N, for calculating collision cross sections
--- START ---

*** TURNING POINT FOR CHANNEL 1 (FOUND IN 15 STEPS) : 2.5034818 (W/DW -0.2718D-12 0.2196D+04 /JFAII 0)***

*** TURNING POINT FOR CHANNEL 2 (FOUND IN 4 STEPS) : 2.21274658 (W/DW -0.8235D-12 0.1755D+04 /JFAII 0)***

*** TURNING POINT FOR CHANNEL 3 (FOUND IN 14 STEPS) : 2.60011350 (W/DW -0.1491D-12 0.1123D+04 /JFAII 0)***

*** TURNING POINT FOR CHANNEL 4 (FOUND IN 18 STEPS) : 3.44367315 (W/DW -0.3347D-13 0.4181D+04 /JFAII 0)***

--- ACTION ---

CHANNEL 1 STARTS AT = 2.5034818 WITH PHASE 0.426645E+04 AND AMPLITUDE 0.100000E+19
CHANNEL 2 STARTS AT = 2.21274658 WITH PHASE 0.022526E+04 AND AMPLITUDE 0.100000E+19
CHANNEL 3 STARTS AT = 2.60011350 WITH PHASE 0.416431E+04 AND AMPLITUDE 0.100000E+19
CHANNEL 4 STARTS AT = 3.44367315 WITH PHASE 0.117000E+04 AND AMPLITUDE 0.100000E+19

***** A matrix A is a matrix in [1.47796 12.06138] in 412 steps

------ A = MATRIX ------

| TOT | 100 ERRD 0.250966D+01 |
| TOT | 2 |

1 2 3 4
1 0 0
2 0.15779-03 0.0
3 0.0 0.21706+05 0.0
4 0.0 0.15000+04 0.0

------ // FREE SHIFTS // ------

0.0144905 0.4425517 0.269452 0.066571

------ END PART OF A MATRIX ------

1 2 3 4
1 0.12597+00
2 0.13118-03 0.55910+00
3 0.03450-03 0.14870-01 0.68710+01
4 0.01321+15 0.9313+11 0.3504+05 0.65115+00

--- END ---

G.G. Buhl-Auri et al. / EDW, for calculating collision cross sections
--- IMAGINARY PART OF S-MATRIX ---

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5454+00</td>
<td>2</td>
<td>0.1616+03</td>
</tr>
<tr>
<td>3</td>
<td>-0.2033+09</td>
<td>1.1589+05</td>
<td>0.5139+00</td>
</tr>
<tr>
<td>4</td>
<td>0.1006+04</td>
<td>6.5610+11</td>
<td>0.3451+05</td>
</tr>
</tbody>
</table>

--- PARTIAL-PARTIAL CROSS SECTIONS (NJ->NJ') ---

<table>
<thead>
<tr>
<th>NJ</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.00</td>
<td>0.1084+03</td>
<td>0.1029+04</td>
<td>0.1129+16</td>
<td>0.1359+27</td>
</tr>
<tr>
<td>3</td>
<td>0.00</td>
<td>0.1716+05</td>
<td>0.1847+00</td>
<td>0.2310+09</td>
<td>0.5310+20</td>
</tr>
<tr>
<td>4</td>
<td>0.00</td>
<td>0.4647+17</td>
<td>0.2465+09</td>
<td>0.8792+01</td>
<td>0.2104+09</td>
</tr>
<tr>
<td>5</td>
<td>0.00</td>
<td>0.3998+29</td>
<td>0.3911+20</td>
<td>0.2174+08</td>
<td>0.4368+00</td>
</tr>
</tbody>
</table>

--- TOTAL CROSS SECTIONS (NJ->NJ') ---

<table>
<thead>
<tr>
<th>NJ</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1646+02</td>
<td>0.1472+00</td>
<td>0.3659+38</td>
<td>0.1255+19</td>
<td>0.4576+11</td>
</tr>
<tr>
<td>2</td>
<td>0.2096+01</td>
<td>0.2902+03</td>
<td>0.3654+04</td>
<td>0.7744+16</td>
<td>0.6175+27</td>
</tr>
<tr>
<td>3</td>
<td>0.3375+04</td>
<td>0.3144+04</td>
<td>0.6663+02</td>
<td>0.8216+04</td>
<td>0.1588+19</td>
</tr>
<tr>
<td>4</td>
<td>0.4627+01</td>
<td>0.2770+04</td>
<td>0.5651+05</td>
<td>0.2159+02</td>
<td>0.6656+08</td>
</tr>
<tr>
<td>5</td>
<td>0.2651+01</td>
<td>0.1109+04</td>
<td>0.6405+00</td>
<td>0.5130+04</td>
<td>0.1272+01</td>
</tr>
</tbody>
</table>

--- TOTAL CROSS SECTIONS (NJ->NJ') ---

<table>
<thead>
<tr>
<th>NJ</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9669+02</td>
<td>0.3664+00</td>
<td>0.3659+04</td>
<td>0.2267+01</td>
<td>0.1937+26</td>
</tr>
<tr>
<td>2</td>
<td>0.7842+01</td>
<td>0.1165+03</td>
<td>0.1604+03</td>
<td>0.8668+14</td>
<td>0.5594+24</td>
</tr>
<tr>
<td>3</td>
<td>0.7788+07</td>
<td>0.1940+03</td>
<td>0.2670+02</td>
<td>0.3786+08</td>
<td>0.9185+18</td>
</tr>
<tr>
<td>4</td>
<td>0.3929+17</td>
<td>0.5397+14</td>
<td>0.3534+06</td>
<td>0.3935+02</td>
<td>0.2930+07</td>
</tr>
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<td>0.6677+24</td>
<td>0.1297+17</td>
<td>0.4312+07</td>
<td>0.4674+31</td>
</tr>
</tbody>
</table>